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PREPARATION AND X-RAY STRUCTURE OF $\text{Cp}_2\text{Ti}(\text{Ph}_2\text{SiH}_2)(\text{PMe}_3)$

Esther Spaltenstein, Pilar Palma, Kristina A. Kreutzer, Christopher A. Willoughby, William M. Davis and Stephen L. Buchwald*

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Abstract: The synthesis and X-ray structure determination of the novel complex, $\text{Cp}_2\text{Ti}(\text{Ph}_2\text{SiH}_2)(\text{PMe}_3)$, **4** is reported. The spectroscopic and structural data indicate that **4** is best described as being a hybrid between a titanium(IV)(silyl)hydride complex and a titanium(II) silane complex. Complex **4** reacts reversibly with N_2 to form the bridging dinitrogen complex **5** and, in the presence of norbornene, **4** catalytically dimerizes Ph_2SiH_2 in quantitative yield.

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Technical Report No. 7

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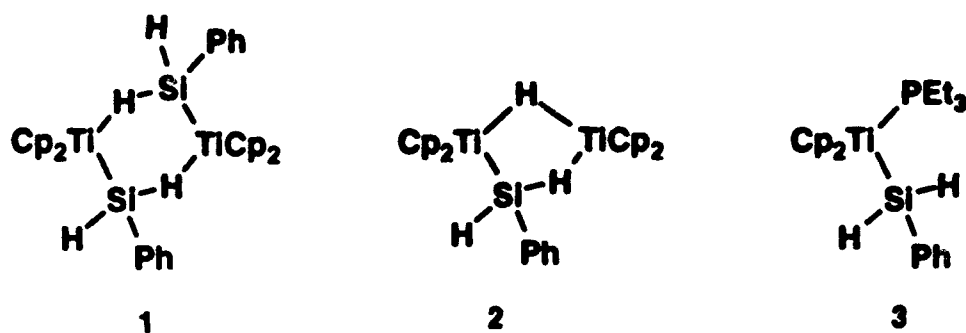
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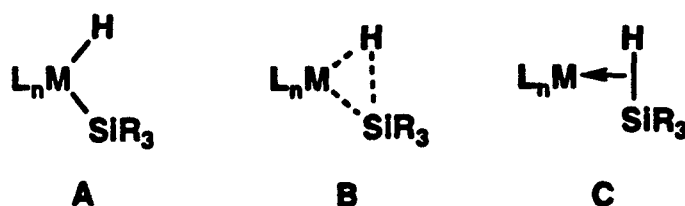
Transition metal(silyl)hydride complexes have been proposed as intermediates in the catalytic hydrosilylation of olefins¹ and the polymerization of organosilanes.^{2,4,6} Several of these complexes have been prepared and studied in detail.³ Harrod and coworkers have isolated and characterized several dinuclear⁴ and mononuclear⁵ titanocene complexes from the reaction of dimethyltitanocene and phenylsilane (Figure 1). The compound $\text{Cp}_2\text{Ti}(\mu\text{-Si}(\text{H})_2\text{Ph})(\mu\text{-H})\text{TiCp}_2$ **2**, is of particular interest and can be viewed as being composed of a titanocene(hydrido)silyl complex and a titanocene. It has been suggested that the titanocene silyl hydride monomer is an active participant in silane polymerization.⁶

Figure 1 Representative Titanium(silyl)hydride Complexes

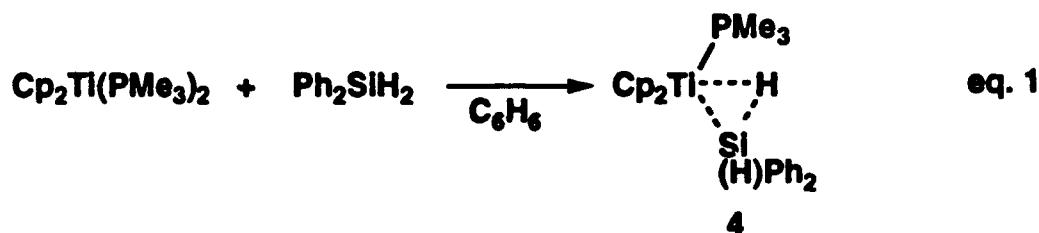


The bonding in transition metal(silyl)hydride complexes has classically been described by either of two limiting structures, **A** or **C** (Figure 2). However, there are many complexes that cannot be accurately described by either **A** or **C** and are thus best represented by an intermediate structure such as **B**.^{3a} We have previously reported the synthesis of some group 4 silyl hydride complexes, $\text{Cp}_2\text{M}(\text{H})(\text{SiR}_3)(\text{PMe}_3)$, $\text{M}=\text{Zr}, \text{Hf}$.⁷ The physical data for these complexes indicate that they are true metal(silyl)hydride complexes (structure **A**). In this paper we report the preparation and characterization of a novel titanocene complex, $\text{Cp}_2\text{Ti}(\text{Ph}_2\text{SiH}_2)(\text{PMe}_3)$, which, in our view, has a hybrid structure like **B**.

Figure 2 Bonding in Transition Metal(silyl)hydride Complexes



Treatment of a benzene solution of $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ ⁸ with diphenylsilane followed by addition of cold hexanes caused precipitation of an air and moisture sensitive yellow solid identified as $\text{Cp}_2\text{Ti}(\text{Ph}_2\text{SiH}_2)(\text{PMe}_3)$, **4** (eq. 1). Compound **4** was obtained in 63 % isolated yield after washing with hexane. Complex **4** is unstable in solution and decomposes to the dinuclear species $\{(\mu-(\eta^1:\eta^5\text{C}_5\text{H}_4))(\text{Cp})\text{Ti}(\text{PMe}_3)\}_2$ ⁹ and Ph_2SiH_2 . However, in the presence of excess Ph_2SiH_2 , benzene solutions of **4** are stable for several days.

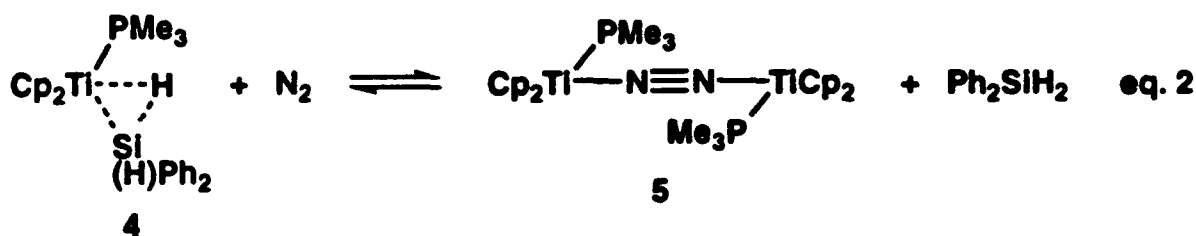


The ^1H NMR spectrum (300 MHz, C_6D_6) of **4** at room temperature exhibits a broad resonance at 6.36 ppm assigned to the silicon hydride and a broad doublet at -3.93 ppm assigned to the titanium hydride. At -55 °C in THF-d_8 (500 MHz) these resonances are completely resolved, the Si-H resonance is located at 6.03 ppm as a doublet of doublets ($J_{\text{HH}} = 11$ Hz, $J_{\text{HP}} = 4$ Hz) while the Ti-H signal is observed at -4.14 ppm, also as a doublet of doublets ($J_{\text{HH}} = 11$ Hz, $J_{\text{HP}} = 68$ Hz). The Ti-H resonance is 3.87 ppm up field of that for the corresponding zirconium complex,⁷ reflecting the more electron rich character of the metal in **4**. In comparison, the Ti-H resonance for the recently reported titanium(IV) hydride, $(^t\text{Bu}_3\text{SiO})_2(^t\text{Bu}_3\text{SiNH})\text{TiH}$, is at 8.62 ppm.¹⁰

The ^{29}Si NMR spectrum of complex **4** (99 MHz, THF-d_8 , -50 °C) shows a doublet of doublets indicating coupling of the silicon to two hydrogens¹¹ ($J_{\text{SiH}_1} = 28$ Hz, $J_{\text{SiH}_2} = 161$ Hz). The large silicon hydrogen coupling constant of 161 Hz is consistent with those found in normal silanes (150 - 200 Hz)^{3a} while the smaller value of 28 Hz is slightly larger than values typically observed for silyl-hydride complexes in which there is no interaction between Si and H ($J_{\text{SiH}} < 20$ Hz).^{3a} This suggests the possibility of a 3 center interaction between the titanium hydride, the titanium and the silicon atom. Consistent with this hypothesis is the large H-H coupling constant of 11 Hz. For the corresponding zirconium analog, $\text{Cp}_2\text{Zr}(\text{H})(\text{SiPh}_2\text{H})(\text{PMe}_3)$,^{1d,7} in which a 3 center interaction is not present, the H-H coupling

constant is 3 Hz. The IR spectrum displays a weak Ti-H stretch at 1508 cm^{-1} ($\nu\text{ Ti-D} = 1042\text{ cm}^{-1}$). This value is slightly lower than that reported for the only other known titanocene (IV) hydride, $\text{Cp}_2^*\text{TiH}_2$ ($\nu\text{ Ti-H} = 1560\text{ cm}^{-1}$)¹² and slightly higher than the value reported for the titanocene (III) hydride $[\text{Cp}^*\{\text{C}_5\text{Me}_4\text{CH}_2(\text{C}_5\text{H}_3\text{N})\}\text{TiH}]$ ($\nu\text{ Ti-H} = 1475\text{ cm}^{-1}$).¹³ The IR stretch for $(^t\text{Bu}_3\text{SiO})_2(^t\text{Bu}_3\text{SiNH})\text{TiH}$ is observed at 1645 cm^{-1} .¹⁰

The silane moiety in complex **4** is only weakly bound and is readily displaced by dinitrogen according to equation 2, leading to formation of the previously reported dinitrogen complex **5**.¹⁴ Under vacuum, nitrogen can be removed to regenerate **4**.



In order to achieve a more complete bonding picture, complex **4** was examined by X-ray crystallography. Importantly, the hydrogen atoms were located and anisotropically refined. The ORTEP drawing of complex **4** is shown in Figure 3, selected bond distances and angles are listed in Table 1.

Figure 3 ORTEP drawing of $\text{Cp}_2\text{Ti}(\text{Ph}_2\text{SiH}_2)(\text{PMe}_3)$, **4**

Table 1 Some Selected Bond Distances and Angles for $\text{Cp}_2\text{Ti}(\text{Ph}_2\text{SiH}_2)(\text{PMe}_3)$, **4**.

Bond Distances, Å		Bond Angles, deg	
Ti-H ₁	1.81 (5)	Si-Ti-H ₁	44 (2)
Ti-Si	2.597 (2)	Si-Ti-H ₂	112 (2)
Ti-P	2.550 (2)	Si-Ti-P	111.78 (7)
Si-H ₁	1.69 (5)	H ₁ -Si-H ₂	156 (2)
Si-H ₂	1.56 (5)	C ₂₀ -Si-H ₁	92 (2)
		C ₂₀ -Si-H ₂	100 (2)
		C ₉ -Si-H ₁	94 (2)
		C ₉ -Si-H ₂	103 (2)
		C ₉ -Si-C ₂₀	105.4 (3)
		Ti-Si-C ₉	118.2 (2)

The Ti-H bond of 1.81 Å is 0.11 Å longer than that of a terminal Ti(III)-H bond in $[\text{Cp}^*(\text{C}_5\text{Me}_4\text{CH}_2(\text{C}_5\text{H}_3\text{N}))\text{TiH}]$ (Ti-H = 1.70 Å)¹³ but well within the normal range of 1.66 to 1.97 Å found for bridging titanium hydrides.^{4,15} The Ti-P distance (2.550 Å) is in good agreement with that of the dinitrogen complex **5** (2.539 Å)¹⁴ and 0.1 shorter than that of complex **3** (Figure 1, Ti-P = 2.651 Å)^{5a} (the longer bond in this complex may be due to greater steric crowding of the more bulky PEt_3 ligand). The Ti-Si distance of 2.597 Å is similar to that of other titanocene silyl derivatives which are typically between 2.60 and 2.63 Å.^{4,5}

A most interesting feature of the structure is the geometry of the silicon atom. This geometry is best described as a distorted trigonal bipyramid with the two hydrogen atoms occupying the apical positions and Ti, C₂₀ and C₉ defining the equatorial plane. The silicon atom is displaced from the equatorial plane toward H₂ with C₂₀-Si-H₂ and C₉-Si-H₂ being 100° and 103° respectively. The Si-H₂ distance of 1.56 Å is 0.09 Å longer than the terminal Si-H distance in the related complex **2** (Figure 1, Si-H = 1.47 Å),⁴ likely due the trans influence of the H₁ ligand. The Si-H₁ distance of 1.69 Å is substantially (15 %) longer than the typical Si-H distance (1.47 Å) but still short enough for an interaction with the silicon atom.^{3a}

The Si-Ti-H₁ angle of 44° is 10° smaller than that of the related zirconium complex $\text{Cp}_2\text{Zr}(\text{H})(\text{SiPh}_3)(\text{PMe}_3)$ ⁷ while the Si-Ti-P angle of 111.78° is roughly the same as that found in $\text{Cp}_2\text{Zr}(\text{H})(\text{SiPh}_3)(\text{PMe}_3)$ (Si-Zr-P = 112.68°). The similarity of the Si-M-P angle in these two complexes indicates that the smaller Si-Ti-H₁ angle is not due to steric crowding resulting from the smaller size of the titanium atom. The smaller Si-Ti-H₁ angle thus reflects a bonding interaction between silicon and H₁.

Since complexes similar to **4** have been implicated in the catalytic polymerization of organosilanes,⁶ we investigated the use of complex **4** as a catalyst for this reaction. When a solution of **4** is treated with excess Ph_2SiH_2 , no reaction is observed. However, in the presence of norbornene, complex **4** catalytically and quantitatively converts Ph_2SiH_2 to the dimer, $[\text{Ph}_2\text{Si}(\text{H})]_2$. This reaction is complete within 1 hour at 45 °C and no induction period is observed. Furthermore, no olefin hydrosilylation^{1d, 6} is observed.

In summary, we have prepared and characterized the first adduct of $\text{Cp}_2\text{Ti}(\text{PMe}_3)$ and diphenyl silane. Both the spectroscopic and structural data suggest that there is a 3 center interaction between the silicon, the titanium and the hydride ligand. The bonding in complex **4** is best described by the intermediate structure **B** (Figure 2). While not totally unambiguous, the low Si-H₁ coupling constant as well as the structural data (short Ti-Si distance and long Si-H₁ distance) indicate that **4** has more character of a metal(silyl)hydride complex (structure **A**) than of a metal silane complex (structure **C**).

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Supplementary Material Available: Detailed experimental procedures for the preparation and spectroscopic characterization of Complex **4**, along with tables of bond distances, bond angles and final positional and thermal parameters for **4** (32 pages).

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